Hydrocarbons of Cigar Smoke

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S. Osman[1] and J. Barson[2]

Eastern Regional Research Laboratory[3]
Philadelphia, Pennsylvania, U.S.A.

Introduction

In a continuing study of the chemical constituents of cigar smoke condensate (for previous publications see Osman *et al.*, 1962 and Osman and Barson, 1964) we have initiated an investigation of the neutral compounds therein. The neutral fraction has been separated into three subfractions: "polar" neutrals, low boiling hydrocarbons and high boiling hydrocarbons. The low boiling hydrocarbon fraction will be the subject of this paper. The compounds that have been identified are benzene; toluene; *o*-, *m*-, and *p*-xylene; styrene; ethylbenzene; dipentene; 1,2,4-trimethylbenzene; and *m*- and *p*-ethyltoluene. To our knowledge, this is the first report of the presence of *m*- and *p*-ethyltoluene in smoke condensate. Estimated amounts of these compounds present in the smoke condensate are also reported.

Experimental

Isolation of Low Boiling Hydrocarbons. Five hundred cigars were smoked according to the procedure described by Schepartz (1959, 1960). The traps containing smoke condensate were washed with 350 ml of ether. The ether solution (A) was extracted with 0.1*N* HCl (4 x 50 ml) to remove basic material and then washed with water until the *pH* of the washing was neutral (~6.0). The acidic compounds were removed from the ether solution in a similar manner with 0.1*N* NaOH. The ether solution (B) free of acids and bases was dried over anhydrous sodium sulfate for 24 hours. The dried solution was then concentrated by distillation until the volume was approximately 25 ml at which point an equal volume of petroleum ether (B.P. 38-42°C) was added; distillation was then continued until the head temperature reached 40°C (pot volume about 20 ml). A precipitate which formed on the addition of 50 ml of methanol to the concentrated solution was removed by filtration. Water (5 ml) was added to the filtrate giving a lower polar layer and an upper layer. The lower layer was washed with petroleum ether (3 x 15 ml) and the

[1] *Senior Research Fellow, Cigar Manufacturers Association of America.*
[2] *Junior Research Fellow, Cigar Manufacturers Association of America.*
[3] *Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.*

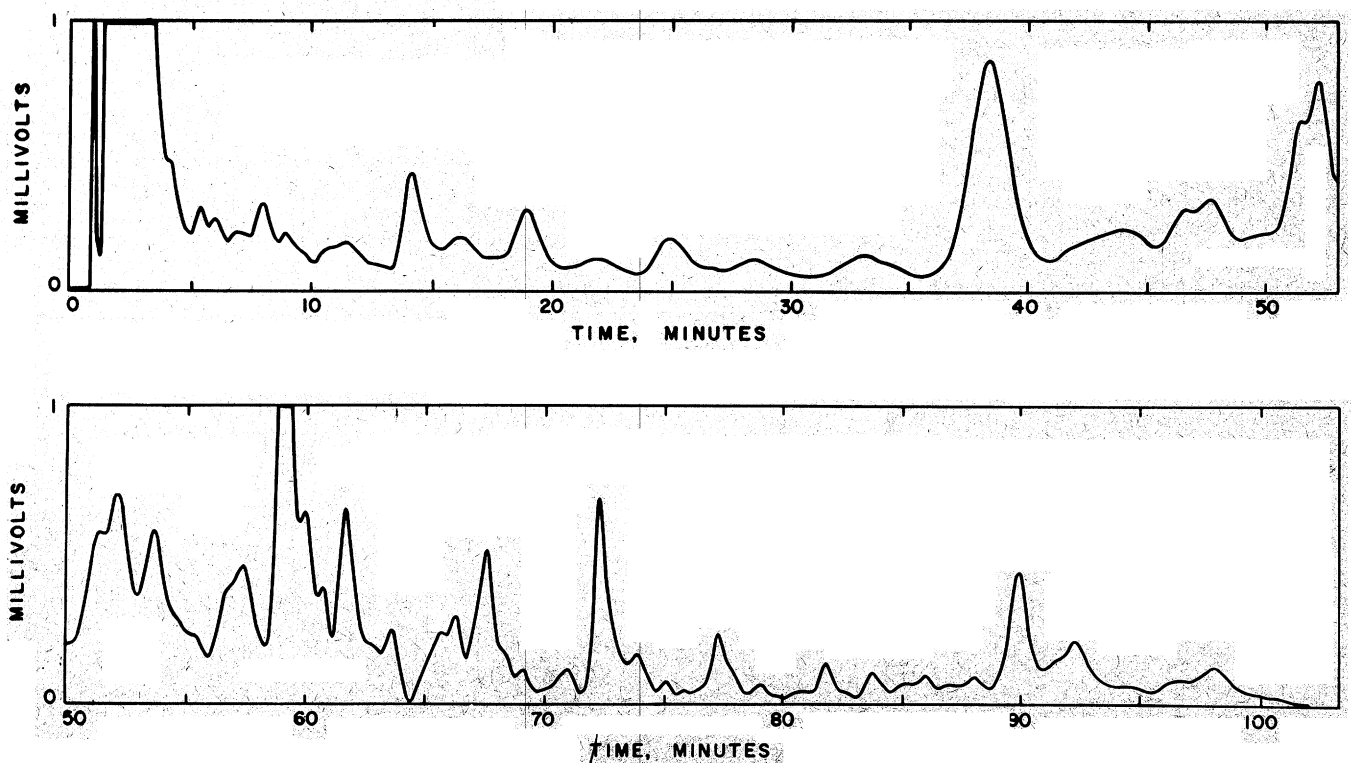

Figure 1. Total neutral fraction of cigar smoke condensate.

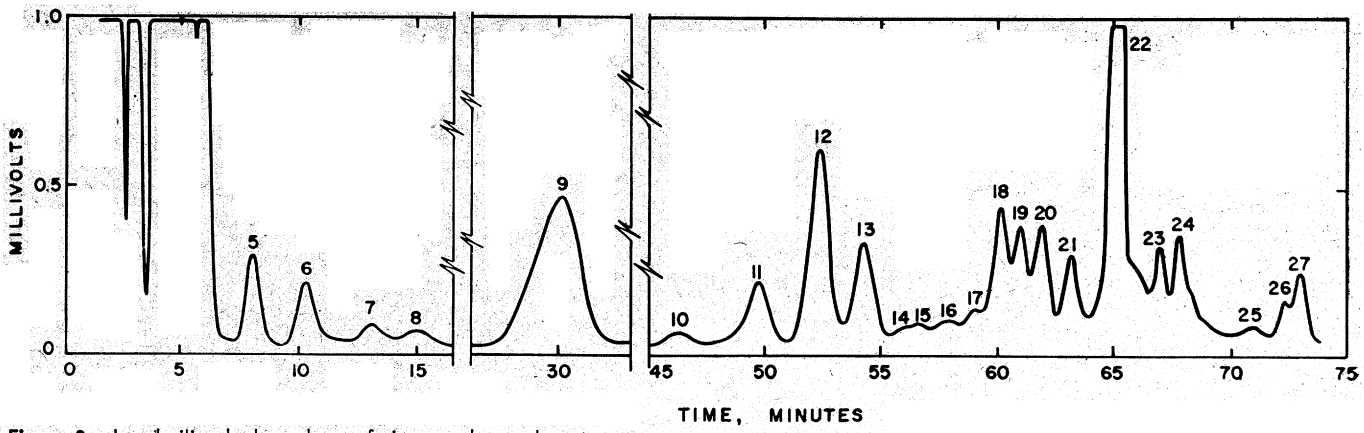

Figure 2. Low boiling hydrocarbons of cigar smoke condensate.

washings were combined with the upper layer, which, in turn, was washed with 90% methanol (10 ml). After drying, an infrared spectrum of this petroleum ether solution indicated the presence of hydrocarbons with no carbonyl or hydroxyl absorption.

The petroleum ether solution of hydrocarbons (C) was distilled from methanol by continuous addition of the latter during the distillation. Distillation was stopped when the distillate no longer clouded upon the addition of water. The distillate was diluted with more water until the methanol to water ratio was approximately 1:1 and then extracted with petroleum ether (6 x 50 ml). The petroleum ether solution was dried and concentrated by distillation to 10 ml (D). The residue from the methanol distillation was taken up in petroleum ether and treated in the same manner to give a high boiling hydrocarbon fraction (E).

To monitor the changes in composition during the above fractionation gas chromatographic analyses were performed on fractions B, C, D and E using an Aerograph A-350[4] fitted with dual thermal conductivity detectors. The column (10 ft × ¼ in) contained Chromosorb W (60-80 mesh) coated with Carbowax 20M (20%). The temperature of the column was maintained at 62°C for the initial 34.5 min. of the run and then programmed to 240°C at a rate of 4° per min.; the temperature was held at 240°C for the remaining time of the analysis (30 min). Injector and detector temperatures were 260°C for the total analysis time and the helium flow rate was set at 60 ml/min at 62°C column temperature.

Further analysis of D was conducted under the same conditions described above with one exception: the columns (10 ft × ¼ in) contained Apiezon L (20%) coated on firebrick.

Identification of Components of Solution D. Three criteria of identification were employed: co-chromatography with known compounds and infrared and ultraviolet spectral analyses. Co-chromatography was run under the set of conditions outlined in the previous section using both columns. For infrared and ultraviolet analyses, eluates of the corresponding chromatographic peaks were collected in U-shaped tubes submerged in a Dry Ice acetone bath. Infrared spectra were obtained on a film of pure eluate contained in a 0.01 mm capillary cell. A solution of the sample in isooctane was used for ultraviolet analysis.

Quantitative Analysis. A gas chromatographic analytical method was employed. Area-concentration relationships were established through the use of knowns corresponding to those compounds identified. All analytical work was done on the Apiezon L column under the conditions previously described. To determine the efficiency of the isolation procedure a control experiment was run. Fifty cigars were smoked, the smoke condensate was removed from the traps with ether, and the ether solution was divided into two equal portions. One half of a 10 ml ether solution containing 30 μl of benzene, toluene, *m*-xylene and dipentene was added to one portion. Both solutions were treated in the manner previously described for the isolation of the low boiling hydrocarbons.

Results and Discussion

A typical chromatogram of the total neutral fraction is shown in **Figure 1.** Due to the great complexity of this solution further fractionation was obviously necessary. A procedure of isolation, somewhat similar to one described by Johnstone and Quan (1962), was used to yield a fraction of much greater simplicity **(Figure 2).** The fraction was devoid

Table 1. Compounds identified in solution D.

Compound	Peak	Method of Identification* IR	UV	Co-chromatography Carbowax	Apiezon	Other
Benzene	6	+	+	+	+	–
Toluene	9	+	+	+	+	–
Ethylbenzene	11	+	+	+	+	–
m-, *p*-Xylene	12	+	+	+	+	–
o-Xylene	13	+	+	+	+	–
Styrene		+	+	+	+	–
m-, *p*-Ethyltoluene	18	+	+	+	+	–
1,2,4-Trimethylbenzene	21	+	+	+	+	–
Dipentene	22	+	+	+	+	NMR

** Identification by infrared (IR), ultraviolet (UV) and nuclear magnetic resonance (NMR) spectra or by co-chromatography on two substrates using known compounds.*

[4] *Mention of a specific commercial product does not constitute endorsement by the United States Department of Agriculture over similar products not mentioned.*

Table 2. Amounts of various hydrocarbons present in cigar smoke condensate

Compound	μg/cigar*	μg/g tob. smoked**
Benzene	175	39
Toluene	360	90
Ethylbenzene	30	7.5
m-, *p*-Xylene	126	31.5
Styrene)	62	15.5
o-Xylene)		
m-, *p*-Ethyltoluene	77	19.3
1,2,4-Trimethylbenzene	15	3.8
Dipentene	240	60

* *Uncorrected for losses incurred during isolation.*
** *Average weight of cigar was 7.0 g and approximately 4.0 g were smoked.*

of carbonyl compounds (as determined by infrared) and relatively high boiling hydrocarbons. The chromatogram contains about 15 major peaks (not including solvent peaks). Many of these were shown to correspond to a single component and others represented mixtures of two compounds. The compounds identified in this fraction are listed in **Table 1.** Many of these compounds were reported in cigarette smoke by Johnstone and Quan (1962) and Bonnet and Neukomm (1956). To our knowledge, however, *m*- and *p*-ethyltoluene have not previously been reported in either cigar or cigarette smoke condensate. Although not listed in **Table 1,** there was an infrared spectral indication of the presence of 1, 3, 5-trimethylbenzene in peak 20. Six peaks (19, 20, 23, 24, 26, 27) were unidentified although certain structural features could be deduced from the infrared spectra of the eluates. For example the spectrum of peak 19 indicated the presence of terminal unsaturation (907, 990 and 1625 cm^{-1}). The infrared spectrum of peak 20 showed the presence of *exo* and *endo* unsaturation and, possibly conjugation; the ultraviolet spectra (λ max 231) confirmed the possible conjugation. The infrared spectrum of peak 23 was similar in many ways to that reported for 2,4-dimethyl,-4-vinylcyclohexane (Binder *et al.*, 1959). The infrared spectra of peaks 24 and 27 showed no strong olefinic absorption; however, the eluate of peak 27 had a λ max 250 mμ.

It should be emphasized that some, if not all, of the unidentified peaks may be mixtures. Positive identifications were not possible with the limited information available. Grossman *et al.* (1963) have reported the formation of a number of olefins, including dipentene, on pyrolysis of solanesol. Preliminary experiments in our laboratory showed strong similarities (in gas chromatographic behavior and infrared spectral characteristics) between pyrolyzates of crude solanesol and a number of components in this fraction including those corresponding to peaks 19 and 20.

Semiquantitative results for a cigar containing unblended filler are given in **Table 2.** The levels are generally within the range of those reported by Johnstone and Quan (1962) for cigarette smoke. Control experiments indicated that recoveries of the identified compounds from the condensate were as follows: benzene, 30%; *m*-xylene and toluene, 50%; and dipentene, 50%. These results are not unreasonably low in the light of the many operations involved in isolating these compounds.

It should be stressed that, although the amounts given in **Table 2** are necessarily semiquantitative in nature, the reproducibility of the analytical method is sufficient to permit detection of large differences in the smoke of different cigar types.

Acknowledgement

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